



REC'D 26 OCT 2004	
WIPO	PCT



INVESTOR IN PEOPLE

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

EP04/11640

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

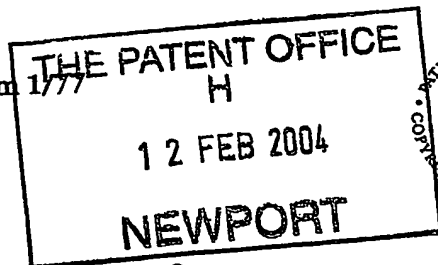
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Stephen Hordley

Dated

16 July 2004



13FEB04 E872878-1 002914
P01/7700 0.00-0403132.4 ACCOUNT CHA

The Patent Office

Cardiff Road
Newport
South Wales
NP10 8QQ

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

1. Your reference	MSP639 GB2		
2. Patent application number (The Patent Office will fill this part in)	0403132.4		12 FEB 2004
3. Full name, address and postcode of the or of each applicant (underline all surnames)	Dow Corning Ireland Limited Unit 12, Owenacurra Business Park Midleton County Cork Ireland Patents ADP number (if you know it) 8556334001 If the applicant is a corporate body, give the country/state of its incorporation Ireland		
4. Title of the invention	Manufacture of Resins		
5. Name of your agent (if you have one)	A M Donlan		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	Dow Corning Limited Intellectual Property Department Cardiff Road Barry CF63 2YL Patents ADP number (if you know it) 414037001		
6. Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7. Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)	Number of earlier UK application	Date of filing (day / month / year)	
8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request?	Yes		
Answer YES if:			
a) any applicant named in part 3 is not an inventor, or			
b) there is an inventor who is not named as an applicant, or			
c) any named applicant is a corporate body.			
Otherwise answer NO (See note d)			

Patents Form 1/77

9. Accompanying documents: A patent application must include a description of the invention.
Not counting duplicates, please enter the number of pages of each item accompanying this form:

Continuation sheets of this form

Description

26

Claim(s) 5

Abstract

Drawing(s)

2 + 2

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for a preliminary examination and search (Patents Form 9/77)

Request for a substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature(s)

A M Donlan



Date 12/02/04

12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

A M Donlan

01446-723740

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 08459 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered YES in part 8, a Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- Part 7 should only be completed when a divisional application is being made under section 15(4), or when an application is being made under section 8(3), 12(6) or 37(4) following an entitlement dispute. By completing part 7 you are requesting that this application takes the same filing date as an earlier UK application. If you want the new application to have the same priority date(s) as the earlier UK application, you should also complete part 6 with the priority details.

MANUFACTURE OF RESINS

[0001] The present application describes a method for making powders, particularly organosilicone resin powders from liquid and gaseous precursors.

5

[0002] Standard processes for making silicone resins generally involve the hydrolysis and condensation of chlorosilanes, alkoxysilanes and silicates, such as sodium silicate. These processes generally require the use of large volumes of solvents with a comparative low concentration of reactive agents in order to prevent/reduce the gelling of the resulting silicone resin products. Due to increasing concerns regarding the environment, industry is aware of a long felt need to avoid the need for the use of such large volumes of solvents wherever possible. One route to achieve this would be through using so-called "dry manufacturing processes" which require minimal and preferably no solvent to manufacture powdered silicone resins. This would reduce environmental concerns and would provide manufacturers with the added incentives of reductions in costs attached to the avoidance for the need to store, use and dispose of and/or recycle large volumes of solvents. In the case of silicone resin manufacture other advantages which would be achieved by avoiding the need for solvents in the resin manufacturing process including the reduction of manufacturing process residence times, which is currently generally caused by the low concentration of reactants present in the reaction mixture, reduction in energy needed to heat reaction vessels, the avoidance for the need of a solvent exchange step to deliver resin products to customers in a liquid delivery medium suitable for the specific application of the customer and the avoidance for the need to have a spray drying step to deliver solid resins.

10
15
20

25 [0003] Silicone resins are generally described using the M, D, T and Q nomenclature in which M units have the general formula $R_3SiO_{1/2}$, D units have the general formula $R_2SiO_{2/2}$, T units have the general formula $RSiO_{3/2}$ and Q units have the general formula $SiO_{4/2}$. Generally, unless otherwise indicated, each R group is normally an organic hydrocarbon group, such as an alkyl group (e.g. methyl or ethyl) or an alkenyl group e.g. vinyl or hexenyl), however some of the R groups may be silanol groups).

30

[0004] Traditional "wet chemistry" processes are generally unable to deliver silicone resin compositions containing various ratio combinations of Q, T, D and/or M groups in discrete particles without gelling, especially in cases where partially functionalised. One particular problem has been the inability to allow the incorporation of wide ranges of organic groups and functionalising groups such as for example amine groups, -OH groups, epoxy groups, and carboxylic acid groups and derivatives such as acid anhydrides, perfluoro groups, acrylate groups and alkylacrylate groups and the like in the resin formulations. Improved control of the particle size ranges, molecular weight and molecular weight distribution are also desirable and not achievable by today's conventional processes.

[0005] Plasma is an at least partially ionised gaseous medium, made of excited, unstable and ionised atoms and molecules and emits visible and UV radiation. When matter is continually supplied with energy, its temperature increases and it typically transforms from a solid to a liquid and, then, to a gaseous state. Continuing to supply energy causes the system to undergo yet a further change of state in which neutral atoms or molecules of the gas are broken up by energetic collisions to produce negatively charged electrons, positive or negatively charged ions. Other species resulting from plasma treatment of a gas include high energy non-charged particles such as gas molecules in excited states, metastable compounds, molecular fragments and or radicals. This mix of excited and charged particles exhibiting collective behaviour is called "plasma", the fourth state of matter. The plasma is electrically neutral and therefore contains positive ions, negative ions and electrons such that the algebraic sum of their charges is zero. The plasma phase is obtained in the laboratory by subjecting a pure gas or a gaseous mixture to external excitation, which is most generally electrical.

[0006] The term "plasma" covers a huge range of systems whose density and temperature vary by many orders of magnitude. Some plasmas are very hot and all their microscopic species (ions, electrons, etc.) are in approximate thermal equilibrium, the energy input into the system being widely distributed through atomic/molecular level collisions; examples include flame based plasmas. Other plasmas, however, particularly those at low pressure (e.g. 100 Pa) where collisions are relatively infrequent, have their constituent species at widely different temperatures and are called "non-thermal non-equilibrium" plasmas.

[0007] In these non-thermal non-equilibrium plasmas, the free electrons are very hot with temperatures of many thousands of Kelvin (K) whilst the neutral and ionic species remain cool. Because the free electrons have almost negligible mass, the total system heat content is low and the plasma operates close to room temperature thus allowing the processing of temperature sensitive materials, such as plastics or polymers, without imposing a damaging thermal burden. The hot electrons create, through high energy collisions, a rich source of radicals and excited and/or unstable species with a high chemical potential energy capable of profound chemical and physical reactivity. It is this combination of low temperature operation plus high reactivity which makes non-thermal equilibrium plasma technologically important and a very powerful tool for manufacturing and material processing as it is capable of achieving processes which, if achievable at all without plasma, would require very high temperatures or noxious and aggressive chemicals.

[0008] Because of their potential in industrial applications atmospheric pressure plasma (APP) systems are of particular interest to industry. APP is a form of atmospheric pressure non-equilibrium plasma and is generated between two parallel electrodes that vary in sizes and configurations but which need to be within several mm distance from each other. Depending on the electrical circuitry and on systems configurations, atmospheric pressure glow discharge (APGD) and/or dielectric barrier discharge (DBD) plasmas are generally produced. Advantageously, when compared to many plasma-based systems currently available, APP operates at about atmospheric pressure and at low temperatures low temperatures ($<200^{\circ}\text{C}$ and preferably $<100^{\circ}\text{C}$). However, limitations exist with respect to system geometry, because the plasma is produced in a plasma region between parallel electrodes with very small gaps between electrodes. It is ideally suited to treat flat, thin and flexible substrates like plastic films, textile webs, etc.

[0009] In the case of the preparation of powders using APGD type processes, one problem regarding the geometry of the system is that during the generation of the particles, reacted reagents and/or treated particles may deposit on the electrodes thereby affecting the electrical and chemical properties of the plasma and potentially the duration of usefulness of the electrodes. Furthermore, the use and or preparation of electrically conducting particles

using APGD is difficult as such particles would interact with the electrical field and create filaments or local discharges and potentially adhere to electrode surfaces.

[0010] Recently, new plasma system have been developed which produce plasmas using high gas flows between the electrodes of an electrical system. These gases exit the system in the form of excited and/or unstable gas mixtures at around atmospheric pressure. These gas mixtures are characterized by being substantially free of electrical charged species which may be utilized in downstream applications distant from the gap between the electrodes which generates the plasma. This "atmospheric pressure post plasma" (APPP) has some of the physical characteristics of low pressure glow discharge and APGD including, for example, glow, presence of active light emitting species, chemical reactivity. However, some clear and unique differences exist including the facts that APPP has higher thermal energy, absence of boundary walls e.g. no electrodes, substantial absence of electrically charged species, large choice of gases and mixture of gases, large flow rate of gases.

[0011] US5807615 describes a "post discharge" atmospheric pressure plasma system for depositing e.g. silicon oxide films on metal substrates wherein a "primary" gas is excited by being passed through a plasma and is then mixed with a precursor gas downstream of the plasma. The precursor gas was a silicon containing compound which has not been plasma treated. The precursor gas was excited by interaction with the primary gas resulting in the formation of a film on a substrate surface. The post discharge nature of this system resulted in the substantial absence of any electrically charged species other than in the plasma region between the electrodes. Column 3 lines 33- 40 states that "since the silicon precursor gas has not passed through the apparatus the risk of forming silica powder (or more generally powders of silicon compounds) inside the plasma discharge is consequently eliminated."

[0012] WO 03/086029 which was published after the earliest priority date of the present application describes the preparation of metallic oxides, metalloid oxides and mixed metal oxides within the plasma generated between the electrodes by Glow Discharge Plasma at both low and atmospheric pressures.

[0013] WO 02/28548 describes a process for enabling the introduction of a solid or liquid precursor into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom in order to form a coating on a substrate. The substrate may be a powder. It does not discuss the making of powders by this method.

5

[0014] Metal oxides and metalloid oxides are made by a wide variety of processes. Titanium dioxide for example may be made by mixing titanium ores in sulphuric acid to make titanium sulphate, which is then calcined to produce titanium dioxide. Silicon dioxide or titanium dioxide may be prepared by reacting their respective chloride with oxygen at an elevated temperature. In this method, the reactants are brought to reaction temperatures by combusting a flammable gas such as methane or propane.

10

[0015] The use of thermal-equilibrium plasma processes for the production of the oxides of silicon, titanium, aluminium, zirconium, iron and antimony has been described in US 20020192138 in which a plasma generator producing a temperature of between 3000 and 12000° C is used to oxidize vapours of salts of the above metals and metalloids. Karthikeyan et al., Materials Science & Engineering, A238, 1997 pp. 275 – 286, describe a method for the preparation of alumina, zirconia and yttria using a high temperature plasma jet to melt and spray the feedstock into a reaction system to form nanoparticles by “plasma jet spray pyrolysis”.

15

20

[0016] Whilst there is a large volume of published information relating to the formation of silica or silicone resin based coatings on substrates little effort appears to have been carried out into the preparation of particles using a plasma type system as the electrical discharge means to generate excited and/or unstable gas species in a post discharge phase. Coopes et al., J. of Appl. Polym. Sci., 37(12), 1989, p3413-22 investigated the formation of films at low pressure derived from hexamethyldisiloxane precursors; R. d'Agostino et al., Polymer Preprints, 34(1), 1993, p673-4 describe investigations on the low-pressure deposition of organosilicon thin films (where the organic groups are methyl groups) by PE Chemical vapour deposition (CVD) using $\text{Si}(\text{OEt})_4\text{-O}_2$ and hexamethyldisilazane- O_2 discharges.

25

30

[0017] EP 1090159 which describes the deposition of silicon dioxide films by introducing tetraethyl orthosilicate (TEOS) into the effluent stream of a low temperature (85 to 350°C) atmospheric pressure plasma jet (APPJ); EP 0617142 protected the preparation of silica thin films prepared using an APGD process; JP06-001870 describes the preparation of laminates using low-pressure plasma CVD (<0.2 torr) in which a hard and abrasion resistant coating is by treating hexamethyldisiloxane in O₂ or N₂O at 80°C; JP2002-127294 describes the formation of gas-barrier plastics films and uses a low pressure plasma CVD (50 to 500 mtorr) to form a silica layer; JP 58-223333 describes the fabrication of semiconductor devices with good electrical properties by coating the device with a silicone resin formed by low-pressure plasma polymerisation of silane coupling agents; and JP 11-221517 describes reflective films for automotive lighting applications which include a topcoat film may be formed by low-pressure plasma polymerisation (< 8 x 10⁻² torr) of monomers such as hexamethyldisiloxane and Si(OEt)₄.

[0018] In accordance with the present invention there is provided a method of forming a powder and/or discrete gel particles of a compound selected from the group of a metallic oxide, a metalloid oxide, a mixed oxide, an organometallic oxide, an organometalloid oxide, an organomixed oxide resin, and/or an organic resin from one or more respective organometallic precursor(s), organometalloid precursor(s) and/or organic precursors; comprising the steps of:

- i) passing a gas into a means for forming excited and/or unstable gas species;
- ii) treating said gas such that upon leaving said means the gas comprises excited and/or unstable gas species which are substantially free of electrical charges at a temperature of between 10°C and 400°C;
- iii) introducing a gaseous and/or liquid precursor which has not been subjected to steps (i) and (ii) into said excited and/or unstable gas species in a downstream region external to the means for forming excited and/or

unstable gas, interaction between said precursor and said excited and unstable gas species resulting in the formation of a powder and/or discrete gelled particles; and

iv) collecting resulting powder and/or discrete gelled particles.

[0019] For the purposes of this application a powder is a solid material in the form of nanoparticles, nanotubes, particles, particulates, pellets, platelets, needles/tubes, flakes, dust, granulates and any aggregates of the aforementioned forms. A gel is a typically jelly-like material in the form of a thin film or solidified mass. It is to be understood that the term “electrically charged species” as used herein is intended to mean ions and electrons.

[0020] The means for forming excited and/or unstable gas species at a temperature of between 10°C and 400°C treats gases passing between the electrodes, which gas upon leaving said means comprises excited and/or unstable gas species at a temperature of between 10°C and 400°C which are substantially free of electrical charges. Such excitation is preferably obtained by electrical discharge, for example, of the dielectric barrier discharge type and/or non-thermal equilibrium plasma. However, any other method capable of exciting a gas mixture such as glow discharge, dielectric barrier discharge and/or corona discharge, light radiation assisted e.g. laser, and any high energetic means is falling within the scope of this invention. The excited gas mixture is generated a non-thermal equilibrium plasma and/or dielectric barrier discharge and/or corona discharge under approximately atmospheric pressure conditions (e.g. from about 0.1×10^5 Pa to about 3×10^5 Pa but preferably at a pressure of between from about 0.5×10^5 Pa to about 1.5×10^5 Pa). Such a means is adapted to provide a post plasma discharge region of excited and/or unstable species downstream from and preferably external to the means for forming excited and/or unstable gas species. Henceforth this region will be referred to as “the downstream region”. The downstream region is generally substantially free of charged particles. The operating temperature of the means for forming excited and/or unstable gas species is between 10 and 400°C. Preferably the operating temperatures of such apparatus is from about room temperature (i.e. about 20°C) to about 200°C but more preferably, the method of the present invention will operate

at temperatures between room temperature (20 ° C) and 160° C. Preferably, gas to be plasma treated has a high flow rate of greater than 50 litres/min, preferably in the range of from 50 litres/min to 500 litres/min, more preferably from about 75 litres/min to 300 litres/min through the means for forming excited and/or unstable gas species.

5

[0021] Any equipment suitable for use in producing a downstream region may be used to undertake the method of the present invention. The means for forming the excited and/or unstable gas species may, for example be any means for generating a downstream region which is preferably substantially free of charged species and which is suitable for use in the method in accordance with the present invention. An Atmospheric Pressure Non-Equilibrium Plasma system, particularly an atmospheric pressure glow discharge having a high gas flow rate (greater than 50 litres per minute) is preferred. Many atmospheric pressure based plasma systems such as glow discharge and dielectric barrier discharge (DBD) based systems typically have low gas flow rate systems (under 50 litres/min) in which the plasma is generated between adjacent electrodes and do not provide the downstream region of the type required in accordance with the present invention and as such are unsuitable for the preparation of particles in accordance with the present invention.

[0022] The means for forming excited and/or unstable gas species may alternatively be a dielectric barrier discharge and/or corona discharge system having a high gas flow rate of at least 50 litres/min so as to provide a suitable downstream region, which is preferably substantially free of charged species for treating the precursors in accordance with the method of the present invention. Particularly preferred systems include the so-called plasma jet and plasma knife type systems.

25

[0023] Particularly preferred systems for the present invention are the means for forming excited and/or unstable gas species as described in US 5941448 and/or in the applicant's co-pending application WO 03/085693, when used with a high gas flow rate of greater than 50 litres/min. WO 03/085693 was published after the earliest priority date of the present invention.

30

[0024] The preferred system comprises a concentric cylindrical electrode configuration having an inlet for the introduction of the gas to be excited and an outlet, in the form of a slit, through which excited gas is able to leave the excitation region. The excitation region is substantially the gap between adjacent pairs of concentric electrodes where a plasma is formed and/or dielectric barrier discharge and/or corona discharge occurs. The electrode configuration typically comprises an inner cylindrical electrode and an outer concentric tubular electrode. At least one of the electrodes has a layer of a dielectric material between it and the other electrode. Preferably at least the inner face of the outer electrode is covered with a dielectric material. The slit is provided along most of the axial length of the electrode configuration in order to provide an elongate source of excited and/or unstable gas in the downstream region into which precursor is introduced.

[0025] By adding precursors in the downstream region, which is substantially free of charged species, powdered products in accordance with the present invention may be prepared.

[0026] In such cases a plume is visible substantially immediately external to the exit which is generally considered to be caused by excited and/or unstable species (atoms and molecules) e.g. metastables, giving off energy when returning to their ground state after having been in the downstream region.

[0027] The geometry of the above electrode configuration means that a system of this type offers unique advantages that allow practical, economic, and large-scale production.

[0028] A typical means for forming excited and/or unstable gas species for use in the method of the present invention may comprise an electrode configuration comprising one or more pairs of electrodes between which a plasma is generated and/or dielectric barrier discharge and/or corona discharge occurs in a substantially constant gap of from 1 to 100mm, preferably from 2 to 10 mm between the electrodes. The electrodes being radio frequency (RF) energised with a root mean square (rms) potential of 1 to 100 kV, preferably between 1 and 30 kV and most preferably between 2.5 and 10 kV, however the actual value will depend on the chemistry/gas choice and plasma region size between the electrodes. The frequency is

generally between from 1 to 500 kHz, preferably at 10 to 300 kHz. Preferably, the power used in the apparatus is preferably greater than or equal to 1 W/cm^2 , more preferably greater than or equal to 10 W/cm^2 and most preferably will be between from about 10 to about 100 W/cm^2 (normalised per unit surface area of dielectric).

5

[0029] Metal electrodes may be used and may be in, for example, the form of metallic cylinders, tubes, plates or mesh. The metal electrodes may be bonded to dielectric material either by adhesive or by some application of heat and fusion of the metal of the electrode to the dielectric material. Alternatively one or more of the electrodes may be encapsulated within a dielectric material or may be in the form of a dielectric material with a metallic coating such as, for example a dielectric, preferably a glass dielectric with a sputtered metallic coating.

10

[0030] The dielectric materials may be made from any suitable dielectric, examples include but are not restricted to polycarbonate, polyethylene, glass, glass laminates, epoxy filled glass laminates, ceramics and the like.

15

[0031] The gas used to form the excited and/or unstable gas species which are provided to the downstream region need not comprise noble gases such as helium and/or argon and therefore may be solely air, nitrogen, oxygen, hydrogen or the like and any suitable mixture thereof. Where an oxidising or reducing gas is required to be included in the gas used to form the excited and/or unstable gas species, the gas used may comprise a mixture of, for example, nitrogen with an appropriate oxidising gas such as O_2 , H_2O , CO_2 , CO , nitrogen oxides (such as NO_2), or air and nitrogen with an appropriate reducing gas, e.g. H_2 , CH_4 or NH_3 when a reducing plasma environment is required. However, the selection of gas depends upon the plasma processes to be undertaken. Oxidizing or reducing gases will be used alone or in mixtures, typically with nitrogen in any appropriate mixture such as for example in the case of an nitrogen and oxygen mixture, the mixture may comprise 90 – 99.995% nitrogen and 50ppm to 10% oxidizing or reducing gas. The noble gases, Ar, He, Ne, Xe and Kr may be utilised alone or in combination with oxidising or reducing gases (Ar and/or He being the most preferred) but are expensive and as such are only used if needed. Mixtures of any of the above may also be used where deemed appropriate.

20

25

30

[0032] The introduction of the excited and/or unstable gas species into the downstream region is preferably achieved by passing a gas, at a high flow rate, through the electrode configuration of the means for forming excited and/or unstable gas species as described above, which when a potential difference is applied between the electrodes generates a plasma or dielectric barrier discharge and/or corona discharge between adjacent pairs of electrodes. When a plasma is generated between the electrodes, the gap between the electrodes will contain an ionised gaseous medium, comprising excited and ionised atoms and molecules and will emit visible and UV radiation. Gas having passed between the electrodes and out through the slit comprise an excited and/or unstable gas mixture which is substantially free of electrically charged species as substantially all the charged species will remain in the gap between the electrodes. The visible plume which is observed at the slit is the effect of the excited and unstable atoms and molecules giving off energy when returning to there ground state.

[0033] Whilst gases may be excited due to microwave excitation in the method of the present invention, this is not a preferred option.

[0034] The liquid and/or gas precursor is in the form of a liquid compound, a solution of a high viscosity liquid or solid compound in either a liquid carrier or a liquid co-reactive and/or a molten solid. When using a liquid precursor, the liquid precursor may be entrained on a carrier gas or transported in a vortex or dual cyclone type apparatus, in which case the liquid to be treated may be fed in through one or more inlets within e.g. a fluidised bed. A fluidised or circulating bed in the context of the present invention means a process based on fluidized beds of solid particles, in which the solids, by suspension or agitation, exist in an expanded state with zero angle of repose and assume the shape of the containing vessel. Such fluidized beds may also be known as moving bed, aerated beds, self supporting or boiling beds, bubbling beds and turbulent beds, and when the gas superficial velocities are high enough can also become relatively dilute circulating and transport systems. Fluidisation is generally achieved by pneumatic gas velocity means but can also be assisted by mechanical and sonic means known to those skilled in the art. Transport systems suitable for the present invention

include the fluidized bed systems described in Perry's Chemical Engineer's handbook 6th Ed, 1984 pages 20-59 to 20-77. Ref fig 20-75.

5 **[0035]** In one preferred embodiment of the present invention there is provided a single unit comprising the means for forming excited and/or unstable gas species, an introduction means for introducing precursors into the excited and/or unstable gas and a suitable means of collecting the end product e.g. by way of an electrostatic precipitator, a cyclone, a scrubber, or filter system or the like. Preferably the means for collecting the end product may be positioned
10 away from the downstream region, particularly in cases where the resulting powder and/or discrete gel particles are very fine e.g. nanoparticulate size to manufacture gel or solid particles where the particles float in e.g. a fluidized or circulating bed.

15 **[0036]** Preferably the single unit is a fluidised or circulating bed reactor. Particularly preferred is a system wherein the means for forming excited and/or unstable gas species is positioned such that the gas which is used as the source of excited and/or unstable gas species in the downstream region at the base of the fluidised or circulating bed reactor is also utilised as the gas supporting the fluidised or circulating bed. The use of a fluidised or circulating bed
20 type of system results in excellent mixing and thereby a generally consistent powder and/or discrete gel particle, particle size, which may be substantially predetermined by pre-setting the exposure time of the precursors in the downstream region in the fluidised or circulating bed. The powder circulating in the fluidised or circulating bed will be transportable through both the downstream region and where appropriate through the external plume.

25 **[0037]** Furthermore, the liquid precursor may be maintained stationary in a suitable container which may be fixed in the downstream region, in which case, if required, the means for forming excited and/or unstable gas species may be moved relative to the receptacle. Whichever means of transporting and/or retaining the liquid precursor is utilised, it is
30 preferred that the exposure time in which liquid precursor remains within the downstream region is constant in order to ensure an even treatment throughout the duration of the method in accordance with the present invention.

[0038] Additional gas inlets or exits from external gas sources and/or additional means for forming excited and/or unstable gas species may be positioned anywhere in the fluidised or circulating bed e.g. at the bottom, side or top of the reactor, to assist in suspending particles and/or droplets or the like against gravity. Each of said additional means would utilize the source of gas as the gas for the fluidised or circulating bed. A single acoustic self-oscillating jet plasma head may be utilised to offer dynamic mixing/fluidisation in the fluidised or circulating bed as well as forming a plasma between electrodes.

[0039] Preferably, powder and/or discrete gel particles which are formed in the downstream region in accordance with the present invention (preferably in a fluidised or circulating bed), are prevented by the excited and/or unstable gas in the fluidised or circulating bed from passing through the slit into the electrode configuration and depositing on one of the electrodes. However where appropriate an electrically conducting mesh may be placed in the fluidised or circulating bed external to the electrode configuration, preferably between the external plume and the downstream region. The inclusion of the mesh may serve several purposes, firstly it significantly reduces the opportunity for and preferably prevents powder and/or discrete gel particles obtained in accordance with the method of the present invention, from entering the electrode configuration through the slit and depositing on an electrode surface. Secondly it also substantially prevents any residual charged species from entering the downstream region and thirdly it acts as a means of distribution for the gas being introduced into the fluidised or circulating bed, i.e. it will spread the entry of gas into the fluidised or circulating bed. The electrically conducting mesh may be made from any suitable material but is preferably made from stainless steel, copper or the like.

[0040] In many means for forming excited and/or unstable gas species suitable for use in the method of the present invention there may be substantially no charged species introduced into the downstream region or in the visible plume projecting outwardly from the slit in the electrode configuration. Hence, substantially all charged species/ formed during excitation of the gas passing between the electrodes which generate a plasma and/or where dielectric barrier discharge and/or corona discharge occurs. The visible plume is substantially the effect of high energy neutral particles such as metastable atoms and/or molecules giving

off energy when returning to their ground state. However, other systems may contain charged particles within the visible plume. Preferably the electrically conducting mesh has a voltage applied to it such that it will attract or repel all positively or negatively charged molecules present in the plume and thereby prevent said charged molecules from entering the downstream region in the fluidised or circulating bed.

[0041] In the case where a fluidised or rotating bed is utilised precursor may be introduced into the bed at any appropriate position but is preferably introduced directly into the downstream region(s) of excited and/or unstable gas.

[0042] Alternative reactors which may be utilised for the method in accordance with the present invention include, for example rotating drums, rotary kilns, jet mixers, flat bed reactors (FBR) with recycle/ageing loops, static mixing reactors, sonic mixing reactors, vibrating beds, conveyor belts, tumblers alone or in any suitable combination.

[0043] Preferably ageing and/or recycling loops may be provided. These may be particularly useful when a predetermined particle size is required. Initial particles formed in accordance with the present invention are in the nanoparticle size range and where larger particles are required circulation of such particles back into the bed may be required to build the particles to an appropriate size.

[0044] Particles resulting from the method in accordance with the present invention may be collected by any suitable means for example they may be collected by electrostatic precipitators, filters, cyclones, scrubbers and/or electrophoresis and the like. Other options for collecting the resulting powder and/or discrete gel particle product include a statically electric charged porous plate or a vibrating sieve placed in line with the exit of the powdered particles from the plasma region to collect the resulting powdered particles. Yet another option for collecting the powders and/or discrete gel particles is to bring them into contact with a liquid material which will advantageously be a delivery medium for specific applications.

[0045] The powdered substrate interacts with the excited and/or unstable gas and functionalised precursors in the downstream region. The excited and/or unstable gas comprises high energy non-charged particles such as gas molecules in excited states, metastable atoms and/or compounds, molecular fragments and/or radicals.

5

[0046] The metals, whose oxides and the like this invention particularly relates, are those of columns 3a and 4a of the periodic table, namely aluminium, gallium, indium, tellurium, tin, lead and the transition metals. Hence, metallic oxide products of the present invention may be either single metal oxides such as, for example, the oxides of titanium, zirconium, iron, aluminium, indium, lead and tin, mixed oxides include, for example, aluminium silicate, aluminium titanate, lead bisilicate, lead titanate, zinc stannate, $\text{TiO}_2\text{-ZrO}_2\text{-SiO}_2\text{-SnO}_2$ and a mixed indium-tin oxide. Proportions of mixed oxides may be determined by the ratios of the amounts of each constituent of the precursor to be plasma treated in the method of the present invention.

15

[0047] A metalloid or semi-metal (hereafter referred to as a metalloid) is an element having both metallic and non-metallic properties and is selected from boron, silicon, germanium, arsenic, antimony and tellurium. Preferred metalloid oxide products made according to the method of the present invention are in particular oxides of silicon including silicone resins and the like, boron, antimony and germanium. (It is to be understood that an organometallic oxide, an organometalloid oxide, and an organomixed oxide resin are oxides as described previously which additionally comprise organic groups.)

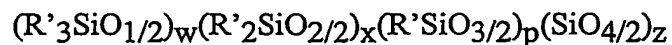
20

[0048] Particularly preferred are the preparation of organofunctional metallic, metalloid and/or mixed oxides resins following the above composition description with the addition of organic groups in the composition for example amino groups, aldehyde groups alkyl halide groups, alkyne groups, alcohol groups, amido groups, carbamate groups, urethane groups, grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA and organic salts, carboxylic acid groups and their derivatives such as acid anhydride groups, organic groups containing boron atoms or phosphorus or sulphur containing groups

25

30

such as mercapto and sulphido groups. In particular a silicone resin having the following empirical formula:-



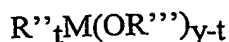
- 5 where each R' is independently an alkyl, alkenyl, aryl, H, OH, or any of the groups described in the previous paragraph and wherein $w + x + p + z = 1$ and $w < 0.9$, $x < 0.9$, $p + z > 0.1$ may be formed by the method in accordance with the present invention.

[0049] Preferably in the method of the present invention precursors are introduced in
10 gaseous or liquid form including molten metals with solids solubilised in a suitable liquid carrier, i.e. a solvent or a liquid co-reactive compound (although wherever possible it is preferred to avoid the use of solvents). Organometallic liquids and gases (although the use of liquid precursors is particularly preferred) of the above listed metals and/or organometalloid liquid precursors of the above listed metalloids are particularly preferred. One of the main
15 advantages of the present invention is that no solvent is usually required and preferably no solvent is used at all, i.e. the organometallic and/or organometalloid gaseous or liquid precursors used in the method of the present invention are solvent-free and the resulting powder and/or discrete gel particle product is made in a solvent free environment, thereby avoiding the need of a solvent exchange step to deliver resin products to customers in a liquid
20 carrier suitable for the specific application of the customer and avoiding the need to have a spray drying step to deliver the silicone resins in a solid form.

[0050] An organic resin obtainable in accordance with the present invention may be any suitable organic resin, for example, polyethylene, polypropylene, polystyrene, polyacrylic
25 acid, polyacrylates, polymethacrylates, polyethylene oxide, epoxy resins, polyvinyl alcohol, polyvinyl acetate, and any organic resins containing phosphorus, halogen containing resins such as for example polyvinyl chloride, polyvinylidene fluoride, nitrogen containing polymers such as for example polyurethane, polyamide, polyimide or sulphur containing resins such as for example polythiophene, polyphenylsulfone.

30 [0051] Preferably in the case of organometallic based precursors, the precursor may for example contain any suitable oxidisable groups including chlorides, hydrides, diketonates,

carboxylates and mixed oxidisable groups for example, di-t-butoxydiacetoxysilane or titanium dichloro diethoxide, titanium diisopropoxide bis(ethyl-acetoacetate) or titanium diisopropoxide bis(tetramethylheptanedionate), but liquid metal alkoxides are particularly preferred. Liquid metal alkoxides suitable for use as precursors in the present invention may, for example, have the following general formula:-



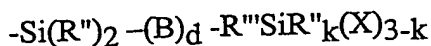
where M is a metal, y is the maximum number of alkoxide groups which may be bonded to the metal, t is 0 or an integer between 1 and y, each R'' group may be selected from alkyl, alkenyl, aryl, H, OH, amino groups, aldehyde groups alkyl halide groups, alkyne groups amido groups, carbamate groups, urethane groups, organic salts, carboxylic acid groups and their derivatives such as acid anhydride groups, organic groups containing boron atoms and phosphorus and sulphur containing groups such as mercapto and sulphido groups and grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA, each R'' is the same or different and is a linear or branched alkyl group having between 1 and 10 carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, pentyl and hexyl. Examples of suitable metal alkoxides include, for example, titanium isopropoxide, tin t-butoxide and aluminium ethoxide. Mixed metallic alkoxides may also be used as liquid precursors, for example indium-tin alkoxides, aluminium titanium alkoxides, aluminium yttrium alkoxides, and aluminium zirconium alkoxides. Metallic-metalloid mixed alkoxides may also be utilised such as for example di-s-butoxyaluminoxytriethoxysilane.

[0052] Similarly organometalloid liquid precursors may contain any suitable groups, which will react in the excited and/or unstable gas into which the precursor is introduced in accordance with the present invention to form the respective oxide or the like, and in particular, in the case of silicon, to form silicon resins, such as alkoxy groups and chloro groups. Examples of suitable metalloid alkoxides include silicon tetramethoxide and germanium tetraisopropoxide. It is to be understood that the term organometalloid liquid as used herein includes polymers of organometalloid elements and in particular in the case of silicon preferably include liquid organosilanes such as, for example diphenylsilane and

dialkylsilanes, e.g. diethylsilane and functionalised silanes containing one or more of the following:- alkenyl, aryl, H, OH, amino groups, aldehyde groups alkyl halide groups, alkyne groups amido groups, carbamate groups, urethane groups, organic salts, carboxylic acid groups and their derivatives such as acid anhydride groups, organic groups containing boron atoms and phosphorus and sulphur containing groups such as mercapto and sulphido groups and grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA.

[0053] Alternatively, the precursor for silicon based powder and/or discrete gel particle products may comprise linear, branched and/or cyclic organopolysiloxanes for the formation of silica and silicates (silicone resins). The linear or branched organopolysiloxanes suitable as liquid precursors for the method of the present invention include liquids of the general formula W-A-W where A is a polydiorganosiloxane chain having siloxane units of the formula $R''_sSiO_{4-s/2}$ in which each R'' independently represents an alkyl group having from 1 to 10 carbon atoms, an alkenyl group such as vinyl, propenyl and/or hexenyl groups; hydrogen; an aryl group such as phenyl, a halide group, an alkoxy group, an epoxy group, an acryloxy group, an alkylacryloxy group or a fluorinated alkyl group and generally s has a value of 2 but may in some instances be 0 or 1. Preferred materials are linear materials i.e. $s = 2$ for all units. Preferred materials have polydiorganosiloxane chains according to the general formula $-(R''_2SiO)_m-$ in which each R'' may be the same or different and is as hereinbefore described and m has a value from about 1 to about 4000. Suitable materials have viscosities of the order of about 0.65 mPa.s to about 1,000,000 mPa.s. When high viscosity materials are used, they may be diluted in suitable solvents to allow delivery of liquid precursor in the form of a finely dispersed atomised spray, or fine droplets, although as previously discussed, it is preferred to avoid the need for solvents if possible. Most preferably, the viscosity of the liquid precursor is in the range between about 0.65 mPa.s and 1000 mPa.s and may include mixtures of linear or branched organopolysiloxanes as hereinbefore described suitable as liquid precursors.

[0054] The groups W may be the same or different. The W groups may be selected, for example, from $-\text{Si}(\text{R}'')_2\text{X}$, or



5

where B is $-\text{R}'''-(\text{Si}(\text{R}'')_2-\text{O})_r-\text{Si}(\text{R}'')_2-$ and

R'' is as aforesaid, R''' is a divalent hydrocarbon group r is zero a whole number between 1 and 6 and d is 0 or a whole number, most preferably d is 0, 1 or 2, k is 0, 1, 2 or 3, X may be the same as R'' or a hydrolysable group such as an alkoxy group containing alkyl groups having up to 6 carbon atoms, an epoxy group or a methacryloxy group or a halide.

10

[0055] Cyclic organopolysiloxanes having the general formula $(\text{R}''_2\text{SiO}_{2/2})_n$ wherein R'' is hereinbefore described, n is from 3 to 100 but is preferably from 3 to 22, most preferably n is from 3 to 6. Liquid precursors may comprise mixtures of cyclic organopolysiloxanes as hereinbefore defined.

15

[0056] In a still further alternative the precursor may comprise a metal hydride, hydroxide, nitride, sulphate, sulphide, oxide hydrate or halide, preferably chloride. Whilst the metal may be any suitable metal, titanium, zirconium, aluminium, tin, indium and mixtures thereof are preferred. Specific examples of using titanium, for example comprise titanium hydride, titanium hydroxide, titanium tetrachloride, titanium nitride, titanium sulphate and titanium oxide hydrate.

20

[0057] The gaseous and/or liquid precursor may also comprise mixtures comprising one or more of the linear or branched organopolysiloxanes as hereinbefore described with one or more of the cyclic organopolysiloxanes as hereinbefore described.

25

[0058] Organic precursors for the preparation of organic resins obtainable in accordance with the present invention may be any suitable organic monomers and/or oligomers for example ethylene, propylene, acrylic acid, acrylates, methacrylates, and any organic precursors containing phosphorus, containing halogens for example vinyl chloride,

30

vinylidene fluoride, containing nitrogen for example urethane, amide, imide or containing sulphur for example thiophene, phenylsulfone.

[0059] The average particle size of the particles formed is preferably from 1 nm
5 (nanometer) to 2000 μm (or micron), preferably between 10 nm and 250 μm .

[0060] When using a liquid precursor, the liquid precursor may be brought into
contact with the excited and/or unstable gas by any suitable means. In a preferred
embodiment the liquid precursor is preferably introduced into excited and/or unstable gas by
10 way of a liquid spray through an atomiser or nebuliser (hereinafter referred to as an atomiser) as
described in the applicants co-pending application WO 02/28548. This provides the invention
with a major advantage over the prior art in that the liquid precursor may be introduced into
the excited and/or unstable gas in the absence of a carrier gas, i.e. a liquid precursor can be
introduced directly into the excited and/or unstable gas by, for example, direct injection
15 directly into the excited and/or unstable gas. Hence, the inventors avoid the need for the
essential features of US 20020192138 that as discussed above requires both very high
working temperatures and the need for the salts to be in a vaporous form.

[0061] Any suitable atomiser may be utilised for the atomisation and introduction of
20 said liquid precursor, examples include the use of an ultrasonic nozzle or pneumatic
nebulisers and nozzles. The atomiser preferably produces a liquid precursor drop size of from
10 nm to 100 μm , more preferably from 1 μm to 50 μm . Suitable atomisers for use in the
method in accordance with the present invention are ultrasonic nozzles from Sono-Tek
Corporation, Milton, New York, USA or Lechler GmbH of Metzingen Germany and
25 Pneumatic nozzles or intersurgical chambers from Clement Clarke International.

[0062] In one embodiment of the present invention the method of the present invention
is used to provide a one-step preparation of functional resins from precursors e.g. silanes with
dry recovery or in liquid carrier suitable for targeted application. In an alternative embodiment
30 there is provided a two step process comprising a first step of making substantially non-
functional resins using the method of the present invention and then a second step in which the
substantially non-functional resins may be functionalised using functionalised precursors by

any appropriate method but most preferably during a further passing of the powder and/or discrete gel particle products from the first step through the downstream region using either dry or wet delivery.

5 [0063] The powder and/or discrete gel particle products produced by the method of the present invention may subsequently be treated as required, using plasma techniques or otherwise, by any suitable process. In particular powder and/or discrete gel particle products made by the present invention may be cleaned and/or activated or coated, for example, by application of a liquid or solid spray through an atomiser or nebuliser as described in the
10 applicants co-pending application WO 02/28548.

[0064] A wide number of possible uses for silicone resins prepared by the method of the present invention are envisaged, these include for example:-
intermediates for modifying viscoelastic properties of siloxane based polymers and
15 elastomers requiring specific properties, in paper coating as release modifiers, and in adhesives, in antifoams and in encapsulant materials for electronic applications; formulated spin-on-glass interlayer dielectrics for use in wafer fabrication (carbon free films); high temperature resistant coatings and carriers for photocopy toners; formulations with organic polymer coatings for thermal stability, weatherability, and surface properties;
20 abrasion resistant coatings (ARC); electronics (IC fabrication, packaging), photonics (waveguide, lenses), traction fluids, tough coating with heat and acid resistance, high performance composites and fire resistant materials applications; and/or flexibility and abrasion resistant auto topcoat in the automotive industry; as a means of providing the silicone benefits to organic systems such as alkyds, epoxy, acryloics, in hot melt sealants,
25 solar encapsulants, and slow curing vinyl resins.

[0065] One perceived advantage with respect to the powder made in accordance with the method of the present invention is that the particle size of the powder made in accordance with the method of the present invention are generally in the nanometre size range
30 (nanoparticles). Hence, powdered particles produced by the method of the present invention may have various utilities, for example they may be useful in the fields of optoelectronics, photonics, solid-state electronics, flexible electronics, optical devices flat panel displays and

solar cells. Silicone resins made by the method of the present invention may be used as high performance composites, fire resistant materials, electrically and/or thermally insulation coatings for example for the microelectronic industry, optically clear coatings and high refractive index coatings for example for the display industry in applications such as
5 televisions, flat panel displays, for the ophthalmic industry in applications such as ophthalmic lenses. Indium-tin mixed oxides are used as electrodes for transparent electrically conductive films and flat panel displays.

[0066] The present invention will now be described further based on the following
10 examples and drawings in which :-

Fig. 1 shows a schematic view of a means for generating excited and/or unstable gas species according to the invention;

15 Fig. 2 schematically shows a fluidised bed adapted to fit the means as shown in Fig. 1

Fig.3 is a detailed schematic drawing of a fluidised bed in accordance with the present invention.

20 [0067] Referring to Fig. 1, Fig 1 shows a means for generating excited and/or unstable gas species 1, having a inlet 2 to a gas homogenisation chamber 3, an inlet 4 for a gas to enter the electrode configuration 15. The electrode configuration 15 comprises an outer electrode 5 an inner electrode 6 and a layer of dielectric material on the inner electrode 7. The gap 9
25 between dielectric 7 and outer electrode 5 is adapted to receive and channel all gas entering inlet 4 from chamber 3 to an excited and or unstable gas species outlet slit 10. Gap 9 is tubular and preferably has an axial length of up to 1 metre but is typically less than 50 cm long. The width of gap 9 is up to 100mm but is preferably less than 10mm. Slit 10 extends over the full axial length of the system.

30 [0068] Electrodes 5 and 6 are connected to a high voltage and high frequency electrical generator 8 operating at a frequency of greater than 15kHz and delivering a power of in the order of 10kW.

[0069] In use a gas to be rendered excited and/or unstable is introduced into homogenisation chamber 3 through inlet 2 and subsequently into the electrode configuration 15. The gas is rendered excited and or unstable whilst in gap 9 wherein it forms a plasma or is subjected to dielectric barrier discharge or corona discharge. The charged species formed within gap 9 remain in gap 9, but the gas comprising excited and/or unstable species leaves configuration 15 through outlet 10 and forms a downstream region 11 in which region it interacts with precursor to form the powder and/or discrete gel particles in accordance with the present invention. A plume 40 is visible to the naked eye and is believed to be the result of previously excited and/or unstable species giving off energy when returning to their ground state after having existed in said excited state for a period of time in the in the downstream region.

[0070] Fig.2 shows an embodiment of the invention where a means 1 in accordance with the invention is adapted for use in a fluidised bed 20, such that gas enters entrance 2 and subsequent to excitation of the type described in relation to Fig. 1 above leaves the configuration through exit slit 10 and enters the fluidised bed 20. The flow rate of the gas passing through means electrode configuration 15 is such that it also acts as the fluidising gas in the fluidised bed 20. The downstream region is identified 11 and the plume is seen at 40 along the exit slit 10.

[0071] Fig. 3 is a more detailed schematic drawing of a fluidised bed in accordance with the method of the present invention including a means of forming excited and/or unstable gas species 1a as described in conjunction with figs. 1 and 2. Alternative and/or additional sites for means of forming excited and/or unstable gas species are identified by numerals 1b and 1c. A means for introducing a liquid precursor 50a is provided at the top of the fluidised bed and an alternative and/or additional means for same is indicated at 50b. Preferably such means 50a and 50b introduce liquid precursor in the form of a liquid spray through an atomiser or nebuliser of the type described in the applicants co-pending application WO 02/28548. A slide valve 56 is provided immediately above the means of forming excited and/or unstable gas species 1a, this is intended as a means of preventing powder and precursor from entering electrode configuration 15 (Fig. 1) once the flow of gas through

means 1 has been switched. This valve may be replaced by the mesh as described previously where appropriate. Waste gases may be removed from the fluidised bed 20 via 52 and are seen to be removable using a pneumatic conveying apparatus at the base of the fluidised bed 54.

5

[0072] In the following examples an M unit is intended to mean $\text{Me}_3\text{SiO}_{1/2}$, a D^{H} unit means $\text{MeHSiO}_{2/2}$, a T units mean $\text{MeSiO}_{3/2}$, a T^{H} units means $\text{HSiO}_{3/2}$ and a Q group means $\text{SiO}_{4/2}$.

10 EXAMPLE 1

[0073] Polymethylhydrosiloxane having a degree of polymerization (dp) of 23 ($\text{M}_{0.11}\text{D}^{\text{H}}_{0.89}$) was continuously fed via a nebulisation nozzle into the plasma reactor and within the post discharge atmospheric plasma secondary phase for a period of 35 min. The reactive gas mixture was 400 ppm oxygen (O_2) in 250 l/min of nitrogen (N_2). The power delivered to the plasma source of the post discharge atmospheric plasma is 2,200 W. A white powder was deposited onto the surface of a polycarbonate support utilised to collect the resulting powder and/or discrete gel particle product. The white powder was recovered and analysed. The powder was found to have a general formula of $\text{M}_{0.04}\text{D}_{0.01}\text{D}^{\text{H}}_{0.68}\text{T}_{0.21}\text{T}^{\text{H}}_{<0.01}\text{Q}_{0.06}$ as determined by ^{29}Si MAS NMR spectroscopy (OH mol % = 13%). Scanning electron microscopy showed the formation of initial particles in the range of few tens of nm that aggregated into larger particles in the range of few tens of microns. The contact angle of a 1 μl water droplet on the resin deposited onto polycarbonate is $> 150^\circ$ showing the resin powder to be superhydrophobic.

25

Example 2:

[0074] Polymethylhydrosiloxane having a dp of 22.6 ($\text{M}_{0.11}\text{D}^{\text{H}}_{0.89}$) was continuously fed via a nebulisation nozzle into the plasma reactor and within the post discharge atmospheric plasma phase for over 35 min. The reactive gas was air at a rate of

30

250 l/min. The power delivered to the plasma source of the post discharge atmospheric plasma was 2,200 W. The white powder deposited onto the polycarbonate support was again recovered and analysed. The composition of the obtained resin was determined as

$M_{0.02}D_{0.02}D^H_{0.04}T_{0.60}Q_{0.34}$ by means of ^{29}Si MAS NMR spectroscopy (OH mol % = 28%).

[0075] The contact angle of a 1 μl water droplet on the resin deposited onto polycarbonate was $> 157^\circ$ showing that the resin powder was superhydrophobic. Particles Size analysis of the white organosilicone resin powder was undertaken using a Coulter LS 230 Laser Particles Size Analyser (from 0.04 to 2000 μm), in isopropanol (IPA), using the Mie theory and the glass optical model calculation for a fluid corresponding to IPA and sample corresponding to glass (real = 1.5 Refractive Index (RI), imaginary RI = 0). The particle size distribution of this organosilicone resin is bimodal from 40 to 600 nm and from 1 μm to 40 μm , both centered at below 300 nm and below 4 μm . The overall particle size distribution is centered (50% in volume) at a particle diameter of below 4 μm .

Example 3:

[0076] A 1:1.2 mixture of 1,3,5,7-tetramethylcyclotetrasiloxane in 1,3,5,7,9-pentamethylcyclopentasiloxane was sprayed via a pneumatic nebulisation nozzle into the plasma reactor and within the post discharge atmospheric plasma phase and thus over 35 min. The reactive gas mixture was 400 ppm oxygen (O_2) in 250 l/min of nitrogen (N_2). The power of the post discharge atmospheric plasma is 2,200 W. The white powder deposited onto polycarbonate was recovered and further analysed. The composition of the resulting resin was found to be $M_{0.02}D_{0.03}D^H_{0.27}T_{0.43}T^H_{0.03}Q_{0.22}$ as determined by ^{29}Si MAS NMR spectroscopy (OH mol % = 17%). The contact angle of water on the resin deposited onto polycarbonate was $> 150^\circ$. Particles Size analysis of the white organosilicone resin powder was undertaken using a Coulter LS 230 Laser Particles Size Analyser (from 0.04 to 2000 μm), in IPA, using the Mie theory and the glass optical model calculation for a fluid corresponding to IPA and sample corresponding to glass (real 1.5 RI, imaginary 0). The

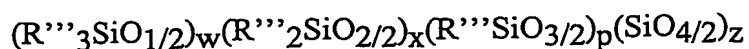
particle size distribution of this organosilicone resin is bimodal from 40 to 600 nm and from 1 μm to 40 μm , both centred at below 200 nm and below 10 μm . The overall particle size distribution is centred (50% in volume) at a particle diameter of below 6 μm .

CLAIMS

- 1) A method of forming a powder and/or discrete gel particles of a compound selected from the group of a metallic oxide, a metalloid oxide, a mixed oxide, an organometallic oxide, an organometalloid oxide, an organomixed oxide resin, and/or an organic resin from one or more respective organometallic precursor(s), organometalloid precursor(s) and/or organic precursors and mixtures thereof; comprising the steps of:
 - i) passing a gas into a means for forming excited and/or unstable gas species;
 - ii) treating said gas such that upon leaving said means the gas comprises excited and/or unstable gas species which are substantially free of electrical charges at a temperature of between 10°C and 500°C;
 - iii) introducing a gaseous and/or liquid precursor which has not been subjected to steps (i) and (ii) into said excited and unstable gas species in a downstream region external to the means for forming excited and/or unstable gas, interaction between said precursor and said excited and unstable gas species resulting in the formation of a powder and/or discrete gelled particles; and
 - iv) collecting resulting powder and/or discrete gelled particles.
- 2) A method in accordance with claim 1 wherein the means to generate excited and/or unstable gas species is an electrical discharge apparatus.
- 3) A method in accordance with claim 1 or 2 wherein the liquid precursor is treated by the excited and/or unstable gas species resulting therefrom, in a container.

- 4) A method in accordance with claim 3 wherein the container is a fluidised bed.
- 5) A method in accordance with claim 4 wherein the gas comprising excited and/or unstable gas species is utilised as the gas in the fluidised or circulating bed for suspending powders, discrete gel particles and/or droplets of liquid.
- 6) A method in accordance with any preceding claim wherein the liquid and/or gas precursor is in the form of a liquid compound, a solution of a high viscosity liquid or solid compound in either a liquid carrier or a liquid co-reactive and/or a molten solid.
- 7) A method in accordance with claim 6 wherein the liquid precursor is introduced into the excited and/or unstable gas species in the form of an atomised liquid.
- 8) A method in accordance with claim 7 wherein the atomised liquid is introduced into the excited and/or unstable gas species by direct injection.
- 9) A method in accordance with any one of claims 1 to 5 wherein the liquid and/or gas precursor is an organometallic compound of titanium, zirconium, iron, aluminium, indium and tin or mixtures containing one or more thereof.
- 10) A method in accordance with any one of claims 1 to 5 wherein the liquid and/or gas precursor is an organometalloid compound of germanium or silicon.
- 11) A method in accordance with claim 10 wherein the organometalloid compound is selected from an organosilane and an inorganic silane where the inorganic groups are selected from halogeno, hydrogeno, or hydroxyl groups, and mixtures thereof.

- 12) A method in accordance with claim 11 wherein the organosilane is a functionalised silane containing one or more of the following organic groups bearing functionalities such as :- alkenyl, aryl, H, OH, amino groups, aldehyde groups alkyl halide groups, alkyne groups amido groups, carbamate groups, urethane groups, organic salts, carboxylic acid groups and their derivatives such as acid anhydride groups, organic groups containing boron atoms and phosphorus and sulphur containing groups such as mercapto and sulphido groups and grafted or covalently bonded biochemical groups such as amino acids and/or their derivatives, grafted or covalently bonded biochemical species such as proteins, enzymes and DNA.
- 13) A method in accordance with claim 10 wherein the organometalloid compound is an organopolysiloxane having a viscosity of from 0.65 to 1000 mPa.s.
- 14) A method in accordance with any one of claims 1 to 5 wherein the liquid and/or precursor is an organic compound or a mixture of organic compounds or a mixture of organic and organosilicon compounds.
- 15) A powder and/or discrete gel particles of a compound selected from the group of a metallic oxide, a metalloid oxide, a mixed oxide, an organometallic oxide, an organometalloid oxide, an organomixed oxide resin, and/or an organic resin, obtainable in accordance with the method in any preceding claims.
- 16) A powder and/or discrete gel particles in accordance with claim 15 having a particle size of from 1 nm to 2000 μ m.
- 17) A powder and/or discrete gel particles in accordance with claims 15 or 16 comprising an organosilicone resin having the following empirical formula:-



where each R''' is independently an alkyl, alkenyl, aryl, alcohol, H, OH, amino groups, aldehyde groups alkyl halide groups, alkyne groups amido groups, carbamate groups, urethane groups, biochemical groups, biochemical species organic salt based group, carboxylic acid groups and their derivatives such as acid anhydride groups, organic groups containing boron atoms and phosphorus and sulphur containing groups such as mercapto and sulphido groups.

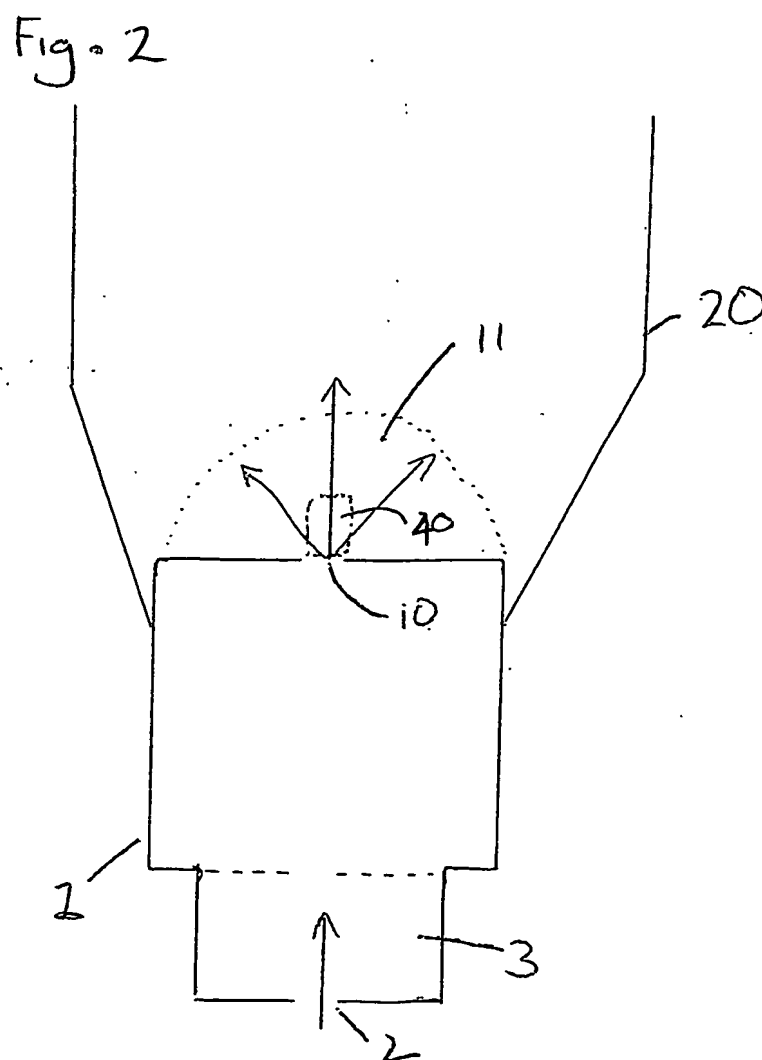
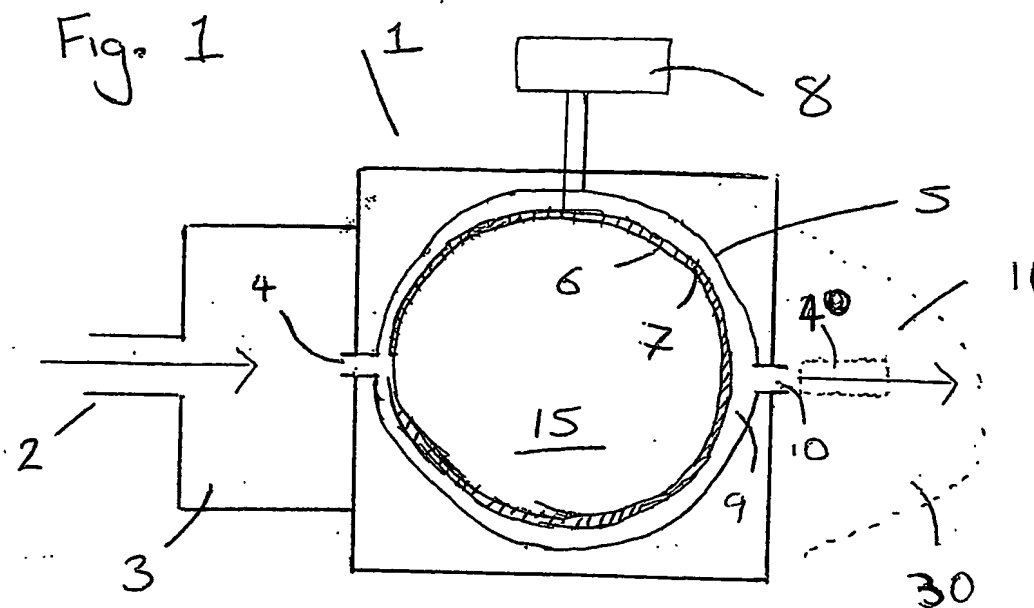
and wherein

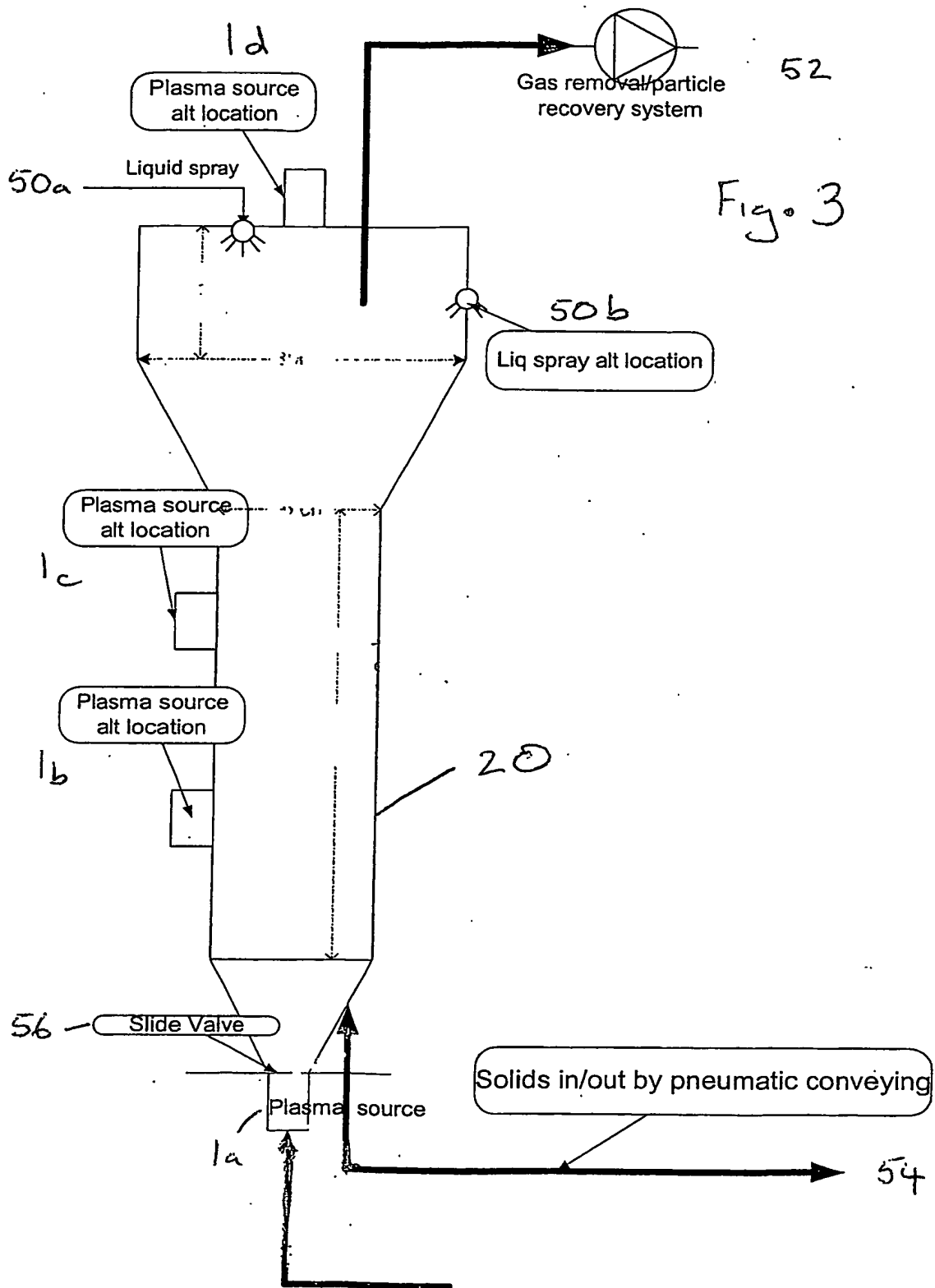
$$w + x + p + z = 1 \text{ and } w < 0.9, x < 0.9, p + z > 0.1.$$

- 18) A powder and/or discrete gel particles in accordance with claim 15 or 16 comprising an organic resin.
- 19) An apparatus for making powders or discrete gel particles by the method of claims 1 to 14 comprising a means for generating an excited and/or unstable gas species, a means adapted to introduce a gaseous and/or liquid precursor which has not been subjected to steps (i) and (ii) into said excited and unstable gas species in a downstream region external to the means forming excited and/or unstable gas, and a means for collecting resulting powder and/or discrete gelled particles.
- 20) An apparatus in accordance with claim 19 wherein said apparatus forms a part of a fluidised or circulating bed.
- 21) An apparatus in accordance with claim 19 or 20 wherein the means adapted to introduce a gaseous and/or liquid precursor is an atomiser.
- 22) An apparatus in accordance with claim 19, 20 or 21 wherein the collection of the resulting powders and/or discrete gel particles is made by bringing them

into contact with a liquid material thus providing a means of directly formulating the powder and/or discrete gel particles into products for specific applications

- 23) An apparatus in accordance with any one of claims 19, 20 or 21 wherein means for generating an excited and/or unstable gas species is an electrical discharge assembly.
- 24. Use of a powder and/or discrete gel particles in accordance with any of claims 15 to 18 in optoelectronics, photonics, flexible electronics, optical devices, transparent electrically conductive films, displays and solar cells or as thermally conductive fillers, biotechnology, biosensors, detergents, filtration, and or separation applications.





PCT/EP2004/011610 *ACE*

